DEVELOPMENT OF POROUS TiO_2 LAYER ON TI6AL4V FOR BONE IMPLANTS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF THE DEGREE OF

BACHELOR OF TECHNOLOGY

IN

BIOMEDICAL ENGINEERING

By

RAVI KUMAR
(Roll No. 110BM0452)

Under the guidance of
Dr. Amit Biswas

Department of Biotechnology and Medical Engineering

National Institute of Technology Rourkela

2014

DEVELOPMENT OF POROUS TIO_2 LAYER ON TI6AL4V FOR BONE IMPLANTS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF THE DEGREE OF

BACHELOR OF TECHNOLOGY

IN

BIOMEDICAL ENGINEERING

By

RAVI KUMAR333
(Roll No. 110BM0452)

Under the guidance of
Dr. Amit Biswas

Department of Biotechnology and Medical Engineering

National Institute of Technology Rourkela

2014

DEPARTMENT OF BIOTECHNOLOY & MEDICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

CERTIFICATE

This is to certify that the thesis entitled, **"Development of porous TiO_2 layer on Ti6Al4V for bone implants"** submitted by **Ravi Kumar** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of requirements for the award of **Bachelor of Technology in Biomedical Engineering at National Institute of Technology Rourkela**. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

……..

Date:
Place: Rourkela

Dr. Amit Biswas
Asst. Professor
Dept. of Biotechnology & Medical Engg.
National Institute of Technology Rourkela

ACKNOWLEDGEMENT

"A Mentor empowers a person to see a possible future, and believe it can be obtained"

I would like to express my deepest gratitude to my project guide, **Dr. Amit Biswas**, Assistant Professor in the Department of Biotechnology and Medical Engineering, NIT Rourkela for believing in me and giving me the opportunity to work under him and lending every support at every stage of this project work. I also owe a debt of sincerest gratitude to **Miss. Sahely Saha** for all the help that I have got from her. This final year project has brought out the best in me and I believe, with this work I have been able to live up to the expectations of all.

Lastly, I would like to thank all the faculty members of our department and everyone in the Biomaterials and Tissue Engineering Laboratory for assisting and motivating me throughout my project work.

Ravi Kumar

Roll No.: 110BM0452

B.Tech (Biomedical Engineering)

National Institute of Technology, Rourkela

ABSTRACT

Titanium and its alloys are among widely used biomaterials, particularly in the field of orthopedics and osteo-synthetic implants. Adhering properties of cells and proteins of the body system on these implants are dependent upon surface chemistry as well as surface morphology of the biomaterial used for making the implant. Anodization is a simple, cost-effective, eco-friendly and promising technique for surface modification. It paves a controlled path to create nano-level roughness and also nano-level features. Surface modification of Ti6Al4V was studied by anodizing a number of the Ti6Al4V alloy samples. Morphological feature was assessed by optical microscope, phase characterization was analyzed by XRD, and the wettability property of the anodically oxidized surface was assessed by contact angle method. The phase analysis carried out by XRD indicated the presence of anatase and rutile in oxidized samples. The oxidized layer was found to be hydrophilic and mechanically stronger than the substrate itself.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

µm	micro meter
nm	nano meter
Ti	titanium
cpTi	commercially pure Titanium
HF	Hydrofluoric acid
TiO_2	Titanium dioxide
H_2SO_4	Sulfuric acid
KCl	Potassium Chloride
HA	Hydroxy Apatite
ECM	Extra Cellular Matrix
V	Volt
M	Molar
Min	Minute
ml	mili liter
^oC	degree Celsius (Temperature)
gf	gram force
hrs	hours
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
HV	Vickers Hardness

CHAPTER 1

INTRODUCTION

INTRODUCTION

Biomaterials are recognized as materials of natural or artificial origin that are used to direct, appendage, replace or support the functions of damaged and/or diseased parts of biological system. There are lots of materials used in the medical field for a wide range of applications ranging from whole replacement of hard or soft tissues (like bone plates, total joint replacement, dental implants, pins, intra-ocular lenses, etc.), augment diagnostic or supportive devices (such as pacemakers, catheters, heart valves, etc.). Biomaterials can be divided generally into metallic, polymeric, ceramic and composite systems. Out of these, metallic biomaterials have been extensively used for the fabrication of surgical and bone-replacement implants. The materials currently used for surgical implants include 316L stainless steel (316LSS), cobalt chromium (Co–Cr) alloys, magnesium & its alloys and titanium & its alloys [1-2].

Titanium and its alloys are widely used biomaterials, particularly in the field of orthopedics and osteo-synthetic implants. This is primarily because of their low density, biocompatibility, resistance to corrosion and mechanical properties [1-4]. Ti6Al4V is by far the most commonly used Ti based alloy having wide range applications in the fields of aerospace, chemical industry, marine and biomedical devices because of their combination of properties in terms of high strength to weight ratio, exceptional resistance to corrosion, and excellent biocompatibility. Ti having strong affinity for oxygen, forms a native layer of oxide when comes in contact with the biological environment. This passive oxide layer has a huge significance in terms of biocompatibility in a biological environment. Ti is inert to the human tissues and on the contrary oxide films are bioactive which help in better osseo-integration. However, the native oxide layer found on the Ti surface is amorphous in nature and therefore possesses low mechanical and biocompatibility property. In order to boost these properties of TiO_2, Ti alloys have been subjected to various methods of surface modification. Through various experiments it has been confirmed that the roughness and porosity of the surfaces play an important role in implant- tissue interaction. Adhering properties of cells and proteins of body system is dependent upon surface chemistry as well as surface morphology of the biomaterial. Several surface modification methods such as, chemical treatment (acid and alkali treatment) [5-8], electrochemical treatment (anodic oxidation) [9], sol–gel [10], ion implantation [11], thermal oxidation [12], etc. have been worked out to obtain TiO_2 surface

without affecting the bulk properties of the material. Nano-tubular layers provide a high surface to volume ratio with controllable dimensions which are able to differentiate mesenchymal stem cells into osteoblast cells [13-14]. Hence a suitable surface chemistry and porosity is required on Ti6Al4V alloy for enhanced biological response on the alloy.

Anodization is a simple, cost-effective, eco-friendly and a promising technique of surface modification. It provides a controlled way to create nano-roughness and even nano-features [14]. Therefore in the present study anodic oxidation of Ti6Al4V has been carried out at fixed temperature with different electrolyte composition, voltage and time duration to observe the nature of oxide form on the surface. The results evidently indicated the presence of two allotropic forms of oxide Ti6Al4V – anatase and rutile in the oxidized layer. The morphological analysis of the oxide layers formed after anodization showed porous microstructure which increased the overall wettability of the oxidized layer.

CHAPTER 2

LITERATURE REVIEW

LITERATURE REVIEW

2.1 MATERIALS

2.1.1 Biomaterial

Any material of natural or synthetic origin that interfaces with living tissue and/or biological fluid and/or illicit desired biological response and used to repair or replace or augment diseased, damaged parts are known as biomaterials. Biocompatibility, the basic requisite for biomaterials, entails the ability of the material to effectively perform producing the pertinent response of the host for the required application. This field of biomaterials research is considered as an elating and challenging one. It is challenging because of the various complexities it faces when biomaterials deals with biological environments for maintaining or restoring tissue and organ function. Various medical devices made of biomaterials such as hip replacements, vascular grafts, assist devices, prosthetic heart valves and the also the implanted drug delivery systems and neurological prostheses [16-20]. Over the ages quite a few materials have been acknowledged for biomedical application. These can be classified generally into metallic, polymeric, ceramic and composite systems. Combinations within same class or between classes have been tried and can be tried again for achieving properties required for specific application. In the past few decades, there has been a considerable increase in accidents where casualties lead to loss of limbs, fractured bones, heart failure etc. Hence, people have opted for orthopedic implants for augmenting the lost parts or recover and revamp their damaged parts.

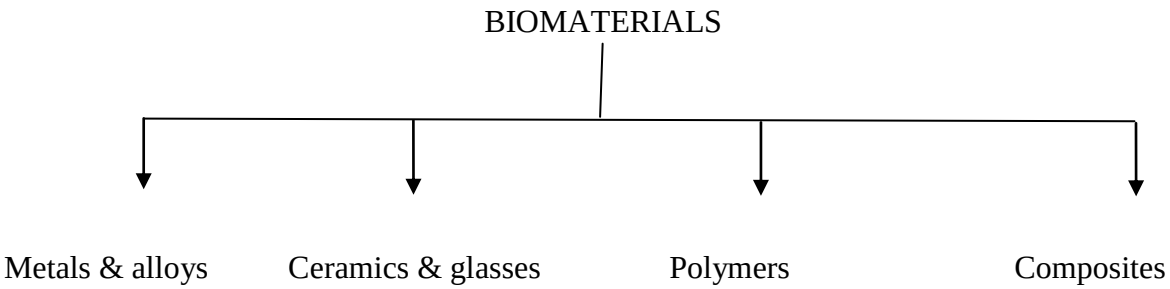


Table 2.1 Different Classes of Biomaterial and their Uses [1]

Class of materials	Current uses
Metals & alloys	
Stainless steel	Joint replacements, bone fracture fixation, heart valves, electrodes
Titanium and titanium alloys	Joint replacements, dental bridges and dental implants, coronary stents
Cobalt-chrome alloys	Joint replacements, bone fracture fixation
Gold	Dental fillings and crowns, electrodes
Silver	Pacemaker wires, suture materials, dental amalgams
Platinum	Electrodes, neural stimulation devices
Ceramics	
Aluminium oxides	Hip implants, dental implants, cochlear replacement
Zirconia	Hip implants
Calcium phosphate	Bone graft substitutes, surface coatings on total joint replacements, cell scaffolds
Carbon	Heart valve coatings, orthopaedic implants
Glass	Bone graft substitutes, fillers for dental materials
Polymers	
Nylon	Surgical sutures, gastrointestinal segments, tracheal tubes
Silicon rubber	Finger joints, artificial skin, breast implants, intraocular lenses, catheters
Polyester	Resorb able sutures, fracture fixation, cell scaffolds, skin wound coverings, drug delivery devices
Polyethylene(PE)	Hip and knee implants, artificial tendons and ligaments, synthetic vascular grafts, dentures and facial implants
Polymethylmethacrylate(PMMA)	Bone cement, intraocular lenses
Polyvinylchloride (PVC)	Tubing facial prostheses
Natural Materials	
Collagen and gelatine	Cosmetic surgery, wound dressings, tissue engineering, cell scaffold
Cellulose	Drug delivery
Chitin	Wound dressings, cell scaffold, drug delivery
Alginate	Drug delivery, cell encapsulation
Hyaluronic Acid	Postoperative adhesion prevention, ophthalmic and orthopaedic lubricant, drug delivery, cell scaffold

Implant devices in general used in human body system to aid healing, correct deformities and restore the lost functions of the diseased or damaged part. The purpose of synthesizing any bio-implant is to provide minimal physiological stress to the remaining body system so that the integrity and functionality of that specific part (say bone in case of orthopedic implant) and prosthetic materials are maintained over a long time period.

2.1.1.1 Ceramics

Ceramics (for example: carbon, alumina, zirconia, bioactive glass and calcium phosphate) are inorganic compounds that have high compression hardness and strength, good corrosion and wear properties and chemically stable in the body environment. The use of ceramic materials is limited due to their low tensile strength and fracture toughness. Their application in bulk form is thus limited to functions where only compressive loads are applied. There is reason for concern about the weak ceramic/metal bond and the integrity of this interface over a lengthy service-period under functional loading.

2.1.1.2 Polymers

Polymers (For example HDPE, PTFE, PLA, UHMWPE, PMMA, Polystyrene, etc.) are long chain molecules having low density, high damping capacity, produces low friction and extremely flexible. They are currently being used for implant applications in various forms such as fibers, textiles, rods and viscous liquids [18]. However, biochemical and mechanical factors of the body environment leads to degradation of polymers which results in ionic attack and forms hydroxyl ions and dissolved oxygen, leading to irritation of tissues and decrease in mechanical properties.

2.1.1.3 Composites

Composites are derived materials obtained by combining advantageous properties of metallic/ceramic/polymeric materials to achieve property which is higher than sum total of individual phase characteristics. There are three distinct classes of composites- Metal-Metal Composite, Polymer-Metal Composite and Ceramic-Metal Composite. It is essential that each component of the composite be biocompatible to avoid degradation between interfaces of the constituents.

2.1.1.4 Metals and alloys Metallic

Metals have reproducible properties such as fabrication, reliability and are rather inexpensive. They are found in a range of stiffness and strength. Their processing can be done to get desired shape and fitting is also easy. Metallic implants are usually made of one of the three types of materials: austenitic stainless steels, cobalt–chromium alloys and titanium and its alloys (Sivakumar *et al* 1992, 1994).Metallic biomaterials made from steel

during early twentieth century turned out to be failures because of detrimental tissue reactions [19]. After 1920, 316 stainless steel gained much popularity as a biomaterial due to its compatibility with biological environment [20]. Currently, most of the artificial joints consist of a metallic component made from either alloys of titanium or Co-Cr. Co-Cr alloys have good wear resistance and due to the formation of stable chromium oxide passive layer which is corrosion resistant. Titanium and its alloys are extremely popular biomaterials in the medical field due to various crucial factors such as strength, biocompatibility, hardness etc. which make them ideal for load bearing applications [20-22]. Ti alloys, particularly Ti6Al4V has now replaced previous biomaterials at load bearing sites because of their enhanced properties over cpTi.

2.2 TI AND ITS ALLOYS (Ti6Al4V)

Titanium and its alloys have a wide range of applications in the fields of aerospace, chemical industry, marine and biomedical devices because of their combination of properties in terms of high strength to weight ratio, exceptional resistance to corrosion, and excellent biocompatibility [21-22] Commercially pure titanium (cpTi) and extra low interstitial Ti6Al4V are the two most commonly used titanium based implant biomaterials [23]. These materials are called biologically inert biomaterials. Usually, they are unchanged when implanted into human bodies. The human body recognizes these materials as foreign and tries to isolate them by encasing them into a fibrous encapsulation. However, they do not promote any adverse reactions and are tolerated well by the human tissues even after encapsulation. These metals do not induce allergic reactions unlike some stainless steels, which have induced nickel hypersensitivity in surrounding tissues.

The commercially pure titanium is very light metal having98.9 - 99.6 % Ti has a density of 4.5 g/cm3. Pure Ti is an allotropic metal having hexagonal α-phase (HCP) below 882 ºC and transforming to a cubic β-phase (BCC) over that temperature [24]. Titanium's light-ness and good mechano-chemical properties are salient features for implant application. There are four grades of unalloyed commercially pure titanium for surgical implant applications. Its very good biocompatibility is due the formation of an oxide film (TiO_2) over its surface. This oxide is a strong and stable layer that grows spontaneously in contact with air and prevents the diffusion of the oxygen from the environment providing corrosion

resistance. The oxide layer has been characterized into various phases (Anatase, Rutile, Brookite). Anatase possesses low hardness and high wettability whereas Rutile form own high hardness and low wettability and high biocompatibility [25-27].

Ti6Al4V is known as the "workhorse" of the titanium industry since it is by far the most commonly used Ti based alloy. The main alloying elements of the alloy are aluminum (5.5~6.5%) and vanadium (3.5~4.5%). This is an (α+β) alloy which generally contain a combination of α-stabilizer&β-stabilizer and is heat treatable to various degrees. Aluminum tends to stabilize the α phase increasing the transformation temperature from α to β phase while vanadium stabilizes the β phase by lowering the temperature of the transformation from α to β [28]. β alloys, which are metastable and contain sufficient β stabilizers such as (Mo, V) completely retain the β phase upon quenching, and it can further be solution treated or aged to achieve significant increase in strength.Ti6Al4V has applications in most of load bearing permanent implants because of their low density, good corrosion resistance, high fracture toughness and fatigue strength and low elastic modulus making it a good bone analogue material. The electrochemical features of integral and protective passivizing oxide layer formed on the alloy during its long term stability in body environment plays a significant role for biocompatibility of implant. Many different types of techniques for modifying surface modification have been created with the objective of improving the bonding at interfaces of the alloy and the bone.

2.3 NEED FOR SURFACE MODIFICATION OF Ti6Al4V

Titanium in its native state is usually protected by a thin, compact Titanium oxide layer. This oxide layer is formed due to exposure to air or any other oxygen containing environment. Typically, the thickness of this passive layer lies between 2-5nm. This layer is responsible for the corrosion resistance property of Titanium and its alloys [1-4]. The oxide layer natively formed is amorphous in nature. Although being biocompatible, this native layer is poor strength and mechanical properties. This may lead to long term failure after implantation. Considering the natural bone as a nano-structured material, a similar type of morphology on implant surface is more favorable for osteo-integration than the conventional Ti implants. In a recent study of osteoblast adherence on both nano-phase and conventional Titanium, it was found that the adhesion was greater on the nano-phase titanium that

possessed more number of grain boundaries on its surface [29].Another important reason for conducting surface modification to titanium medical devices is the specific surface properties that are different from those in the bulk that are generally required. Therefore, in a nutshell surface modification is required on Ti6Al4V implants to

- Obtain orderly arranged TiO_2 microstructure with greater fatigue strength.
- Obtain a surface morphology nearest to human bone for faster recovery.
- Increase the wear resistance and controlled degradability of TiO_2 layer for longer implant life.

Hence, the creation of an optimum micro scales surface roughness, favorable surface chemistry and osteoblast favoring surface morphology is highly required on Ti6Al4V alloy surfaces for fast and enhanced biological response.

2.4 METHODSOF SURFACE MODIFICATION

2.4.1 Surface Modification

Surfaces of commercial implants are found very complicated both with respect to their surface chemistry and morphology. Therefore they are not really well-suited for bridging the gap in our mechanistic understanding of the response of the biological (in vitro and in vivo) environment on the biomaterial surface. This, however, is important in order to design the type of surfaces which direct proper biological response in a particular cell/tissue situation. With the purpose of shortening healing time and minimizing toxic reaction, particular biomaterial/cell architecture at the interface for improving the mechanical properties, reliability, stability and long-term performance of the medical device is highly required. [30]

Several studies have been carried out on the effects of nano-scale and micro-scale roughness on cell behavior, material surface patterning, which allows regionally selective adhesion and growth of cells and their surface chemistry. Materials coated with bio-active layers was examined, specifically those that were created by deposition of Fullerenes, hybrid metal-Fullerene composites, C nanotubes, NCD films, DLC and composite hydrocarbon plasma polymer films enriched with metals. Cell behavior is dependent on the physical and

chemical properties of the surface of the metals. Nanostructured surfaces containing irregularities less than 100nm are seen to mimic nano-architecture of natural tissues. E.g.: nanostructured surfaces preferentially adsorb Vitronectin (due to its relatively small, linear and non-complicated molecules). This protein is recognized by osteoblasts over other cell types. Surface of roughness in tens of nanometers are preferred by bone cells for adhesion, growth, differentiation and phenotypic maturation rather than flat surfaces and surfaces with sub-micron or micro-scale roughness [31].

Surface modification of materials for medical applications presents the possibility of combining the ideal bulk properties (e.g. tensile strength or stiffness for implants, electronic or optical properties for sensors) with the desired surface properties (e.g. biocompatibility or selectivity to a particular bio-molecule). The goal is to exercise a degree of control over the way in which the body or individual bio-molecules respond to the material surface, be it bio-inertness or selectivity. For example, in order to accomplish biological integration, it is required to have good bone formability, in blood-contacting devices, such as artificial heart valves, blood compatibility is crucial. In other applications, good wear and corrosion resistance is also required. Several methods have been devised to achieve this goal.

2.4.2 Methods of Surface Modification of Titanium and its Alloys

The material surface plays an extremely essential role in the response of the biological environment to the artificial medical devices. According to the different clinical needs, various surface modification schemes have been devised. The modification can be achieved by a number of methods:

2.4.2.1 *Changing the surface micro-structure/ topography*

The microstructure and roughness of the material's surface can be modified by techniques such as Grinding, SiC grit- paper polishing, Sand Blasting and Laser-assisted surface melting.

2.4.2.2 *Changing the surface chemistry*

The surface chemistry can be modulated by methods such as Oxidation (chemical, electrochemical, thermochemical), Nitriding (Gas nitriding, plasma nitriding), Carburization, Diffusion process, Ion implantation, Laser surface alloying (LGA, LPA).

2.4.2.3 *Changing the surface chemistry & microstructure*

This includes techniques such as Thermal spray coating, High Velocity Oxygen Fuel (HVOF), Laser cladding, Chemical vapor deposition, Physical vapor deposition, Ion plating, thermal evaporation, sputter coating.

2.4.2.4 *Adding a surface layer or coating*

Glow discharge plasma treatment, Sol-Gel coating, Electrophoretic Deposition.

2.4.3 Electrochemical methods

Anodic oxidation being one of the compositional methods of changing surface chemistry of a material encompasses on electrode reactions in combination with electric field driven metal and oxygen ion diffusion leading to the formation of an oxide film on the anode surface. Anodic oxidation is a well-established method to produce different types of protective oxide films on metals. Different diluted acids (H_2SO_4, H_3PO_4, CH_3COOH and others) can be used as electrolytes in the process [32]. Anodic oxidation can also be used to increase the oxide thickness to increase corrosion protection and decrease ion release, coloration, and porous coatings. The structural and chemical properties of the anodic oxides can be varied over quite a wide range by altering the process parameters, such as electrode potential, electrolyte composition, temperature and current density.

An improvement in bio-activity of Ti is required to enhance the bone-implant bonding ability. This can be achieved by electrochemical anodization of Ti to fabricate Titania nanotube arrays (TiO_2). Nano-tubular layers provide a high surface to volume ratio with controllable dimensions which are able to differentiate mesenchymal stem cells into osteoblast cells [33]. These anodized nano-tubular arrays on Ti surface can be used for drug storage and prolonged drug release. Different geometry of nanotubes can be obtained by using different electrolytes which are aqueous, polar organic or ethylene glycol. The geometry also depends on the voltage applied during anodic oxidation. HA coating on TiO_2 nanotubes can be done using cathodic deposition, electro deposition, and biomimetic deposition. Calcium phosphate deposition on nano-tubular TiO_2 layer can be achieved by electro deposition process.

Several types of experiments have been conducted on anodic oxidation of Ti and Ti6Al4V alloy in chromic media. Two typical experiments of Volta metric (potentio-dynamic) and chrono-amperometric (constant voltage) have been performed [34]. The electrolyte was composed of chromic acid with and without HF. A thin, compact oxide film was formed in the chromic acid electrolyte. A duplex film composed of compact layer surmounted by a columnar porous layer was seen to grow from the fluorinated electrolyte. The Volta metric results indicated a breakdown of the compact film (non-fluorinated medium) for potential around 3V/SCE. It also indicated a strong influence of alloying elements of Ti6Al4V on the formation of porous films in fluorinated medium. The chrono-amperometric results revealed a complex growth process of the porous film. The overall electrochemical efficiency was small and decreased with treatment time.

A recent study revealed reports of fabrication of self-organized TiO_2 nanotube arrays of enhanced surface area prepared by anodic oxidation of a pure Ti sheet in KF and NaF containing electrolyte. The effects of composition and concentration of electrolytes, pH of the solution, anodic potential on the formation and dimensions of the resulting nanotubes were detailed [35]. Nanotube arrays of length greater than 500nm were not possible to obtain with HF containing electrolytes. By adjusting the pH of a KF containing electrolyte to 4.5 using additives such as sulfuric acid, NaOH, sodium hydrogen sulfate, and/or citric acid, increase in the length of the nanotube array to approx. 4.5μm was reported. The prepared nanotubes were found to be composed of amorphous TiO_2, independent of the electrolyte composition. Crystallization of the nanotubes to anatase phase occurred at temperature greater than 280^oC. A transition to rutile phase of the nanotube Ti substrate interface was found to occur at temperature near 480^oC. It appeared that the geometric constraints imposed by the nanotube walls inhibit anatase to rutile transformation. No disintegration of the nanotube array structure was observed at temperature as high as 580^oC. The excellent structural and crystal phase stability of these nanotubes make them promising for both low and high temperature application.

It has been observed by researchers that the major factor contributing to the decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current [35-38]. It has also been reported that under specific sets of conditions highly self-organized titanium oxide nanotubes with significant amount of phosphorous species are formed with diameters varying from approx. 40-100 nm and length from approx.

100 nm to 4μm [39]. The main chemical reaction that occurs during anodization of Ti at the anode can be given by [40]

At the Ti/Ti oxide interface: $Ti \leftrightarrow Ti^{2+} + 2e^-$

At the Ti oxide/electrolyte interface: $2H_2O \leftrightarrow 2O^{2-} + 4H^-$

$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^-$

At both interfaces: $Ti^{2+} + 2O^{2-} \leftrightarrow TiO_2 + 2e^-$

To summarize, anodization or anodic oxidation is a well-established, simple, cost-effective, time-intensive and eco-friendly electrochemical method to modify the surface of titanium and its alloys for better biocompatibility and bioactivity. The anodically oxidized film exhibits a variety of different properties that depend on the microstructure and composition of the materials and processing parameters, such as anode potential, electrolyte composition, temperature, and current. The forth coming chapters comprise of work performed using this method for surface modification of Ti6Al4V alloy samples and subsequent discussions have been made on processing parameters, microstructure and composition of the anodized Ti alloy thus obtained.

OBJECTIVE

The present work is aimed to study the surface morphology, hardness and wettability properties of titanium oxide layer deposited on Ti-6Al-4V surface through the method of anodic oxidation. The objectives to be followed during the course of this entire work are as follows:

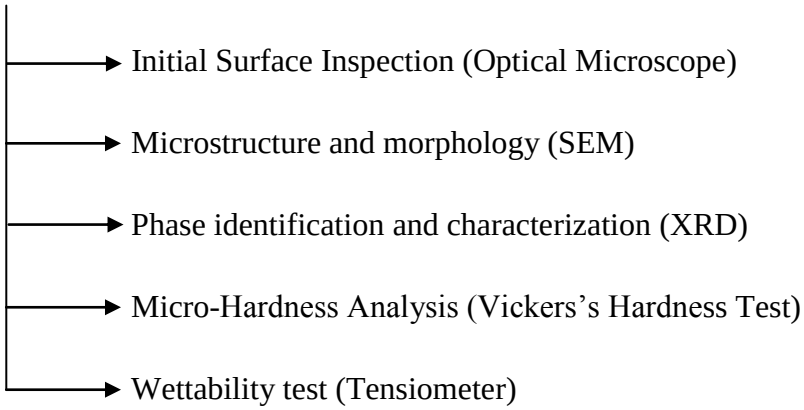
1. Sample preparation

2. Preparation of electrolytic medium

3. Anodic Oxidation of Ti-6Al-4Vsamples

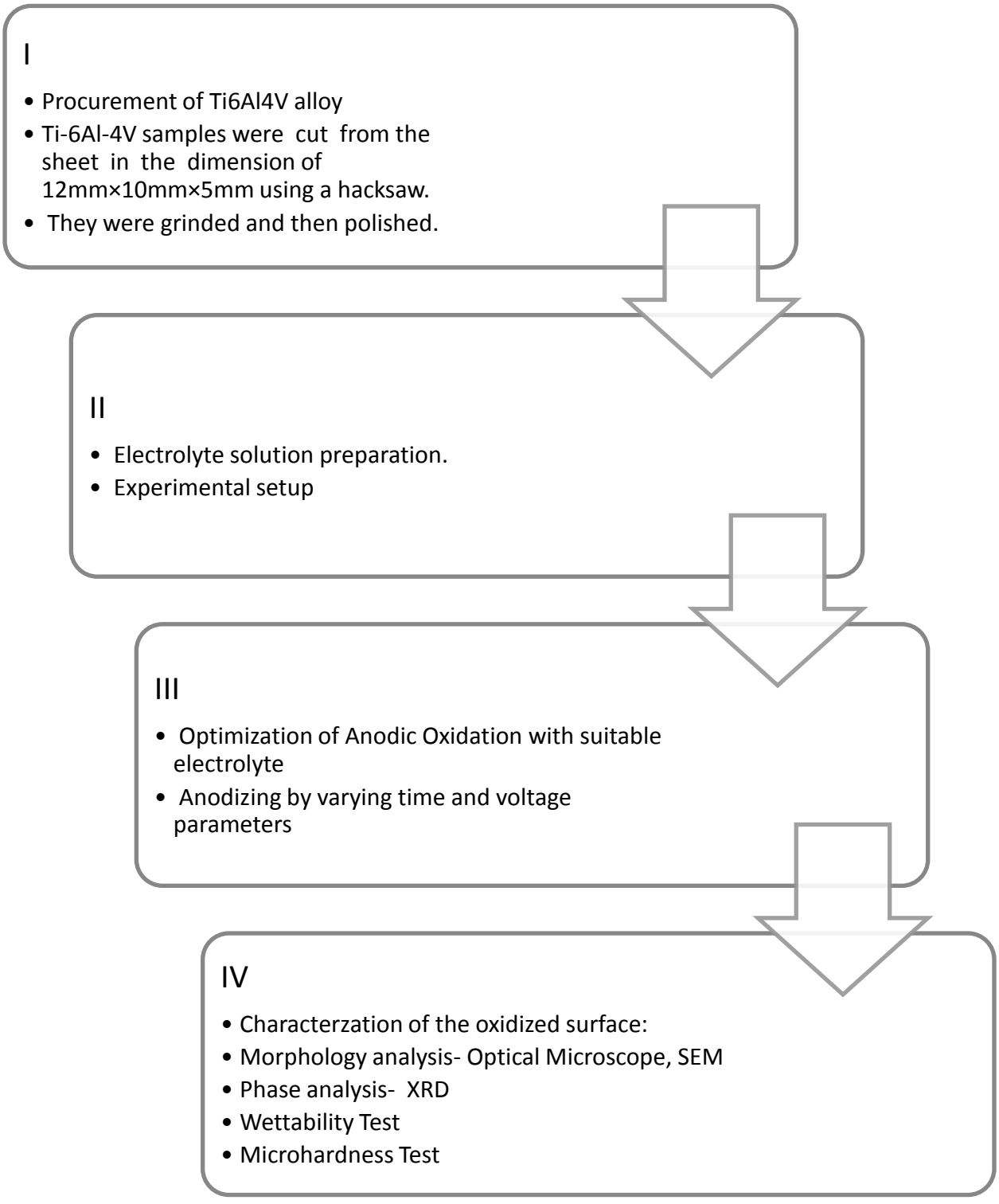
4. Process parameter study of anodic oxidation technique.

5. Characterization Techniques:



6. Biomedical applications and future scope.

Work Progress Flow chart:



CHAPTER 3

MATERIALS AND METHOD

MATERIALS AND CHEMICALS REQUIRED

I. For Sample Preparation

1) Ti6Al4V sheet
2) Graphite electrode
3) SiC grit-papers (grade 1/0, 2/0, 3/0 and 4/0)
4) Hifin Fluid – 'OS'
5) Hydrofluoric acid (48% HF) (RANBAXY Fine chemicals ltd., H2190)
6) Distilled water
7) Acetic acid glacial, L.R (CH_3COOH) (HiMedia Lab. Pvt. Ltd.)
8) Sulfuric Acid (H_2SO_4) (RFCL Limited, S0502)
9) Ethanol (C2H5OH) (Changshu Yangyuan Chemicals, China)

II. For Oxidation &Characterization of Sample Surface

1) Regulated DC power supply (Aplab, LQ6324)
2) Magnetic Stirrer (SPINOT)
3) Air dryer (Orpat)
4) Metallurgical sample saw MS-10 (DUCOM instruments Pvt. Ltd.)
5) Digital multimeter
6) Optical Microscope
7) XRD- PAN Analytical (Philips Analytical, X`Pert)
8) Scanning Electron Microscope
9) Screw Gauge (25X1 mm)
10) Tensiometer (KRUSS GmbH Germany)
11) Digital Camera (Canon PowerShot SX150 IS)
12) LECO Microhardness Tester (LM248AT,LECO corporation, USA)

MATERIALS AND METHODS

3.1 Sample Preparation

- ✓ *Cutting:* A Ti6Al4V sheet was first cut into20 small rectangular shapes for sample preparation.
- ✓ *Grinding:* To remove the native oxide layers, impurities and others contaminations by hydrocarbons form air, these samples were subjected to grinding.
- ✓ *Grit-paper Polishing:* Paper polishing was performed using various grades of SiC abrasive grit-papers (1/0, 2/0, 3/0 and 4/0) for getting a plane and smooth polished surface.
- ✓ *Cloth Polishing:* After grit-paper polishing, the next step was cloth polishing using alumina powder and water on the rotating disk. Then final polishing was done using diamond paste and hifin solution on the rotating disk containing the fine cloth.

This whole polishing procedure gave a mirror finish to the sample surfaces. During the smoothing process abrasive particles get embedded into the metallic matrix of the sample's surface. This phenomenon is commonly termed as abrasive pollution [41]. Therefore for removing this embedded debris, the samples were washed with soap water and cleaned in ultrasonic bath. Finally the samples were dried after rinsing with ethanol. Now, to prevent these samples from getting oxidized by air again, they were wrapped in cotton and then kept in a desiccator. Proper care was taken during polishing so that the extent of plastic deformation would be avoided.

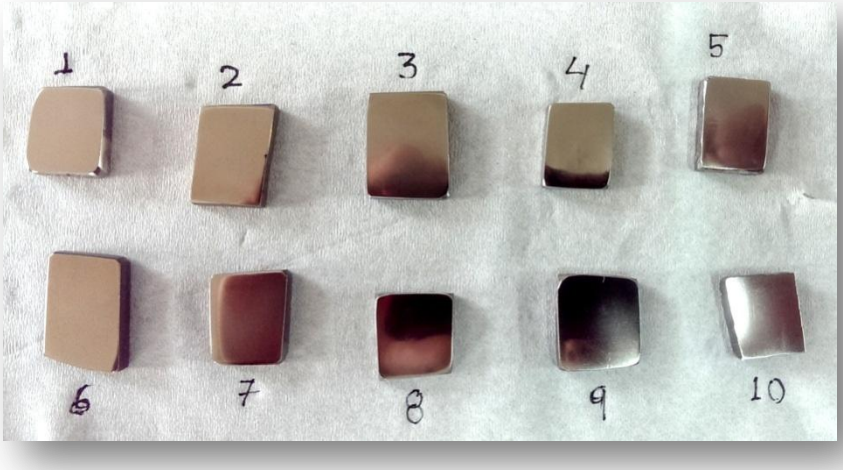


Fig.3.1 Prepared Ti6Al4V samples.

3.2 Preparation of Electrolyte

The first electrolyte used for the anodic oxidation of Ti6Al4V sample was a 0.5M HF in CH_3COOH. For every experiment 100 ml of electrolyte was prepared. The molarity of the available 48% HF was calculated and found to be 23.988M. To prepare a 100 ml solution having 0.5M HF and rest CH_3COOH, amount of 48% HF required was calculated by using the dilution equation ($C_1V_1=C_2V_2$). Therefore, 2.084 ml of available HF was required according to relevant empirical calculations. It was then added slowly to 97.916 ml of CH_3COOH and was stored in a clean 200 ml beaker. Proper safety measures were taken during handling of HF, since it is a highly corrosive acid. Similarly, fresh solutions of 0.5% HF, 1.5% HF and 1M $H_2SO_4$with 0.15% HF were prepared.

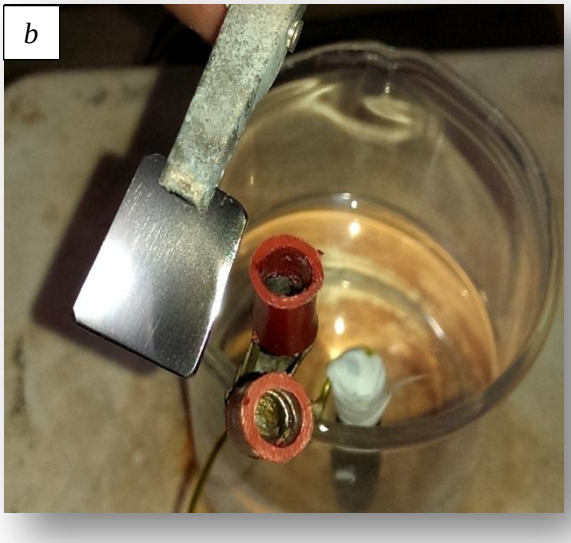
3.3 Experimental Setup

A 2-electrode system was used for the experimental set-up for anodic oxidation of the samples. A beaker was taken as an electrolytic cell. The freshly prepared electrolyte was poured into the beaker. The electrodes were placed carefully inside the medium. The oxidation was carried out using a graphite rod as the cathode and a Ti6Al4V sample as the anode. Wires were connected accordingly. The Ti6Al4V sample connected to the anode was suspended in the electrolyte medium using a clamp stand. The corresponding wires were connected to a DC supply. The DC supply was provided by APLAB regulated DC power supply whose voltage could be modulated between 0-30V. The beaker with electrolyte and electrode was placed on the top of the platform of a magnetic stirrer. A magnet bead was placed carefully into the electrolyte medium, before the beginning of the experiment, to have a slow agitation of the electrolyte which would help in proper circulation of the electrolyte in the beaker. The speed of the rotating magnetic bead was controlled in such a way that the newly formed oxide layer would not get affected by the agitation in the electrolyte. The temperature of the experimental set-up was maintained at constant room temperature. The details of different electrolytes, anodizing voltage and duration of anodization are given in Table 3.1. Once the oxidation was over, the oxidized sample was quickly taken out of the solution and washed in ethanol. It was then dried using a dryer and preserved properly for further analysis.

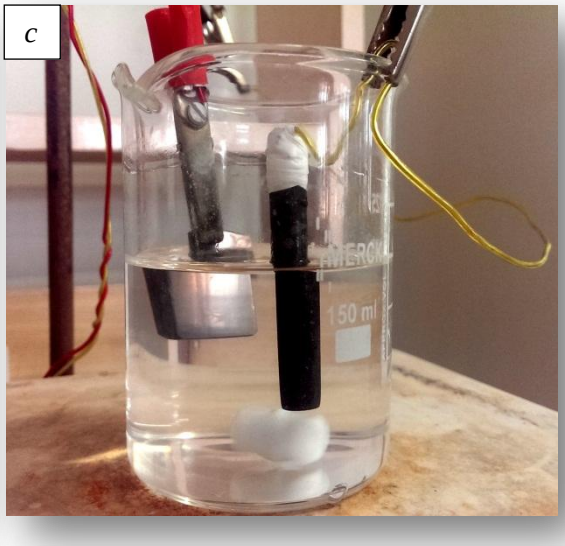
a


Aplab REGULATED DC POWER SUPPLY LQ 6324
11.2V
10.0V
0.00A
HEAT
STIR
SPINOT

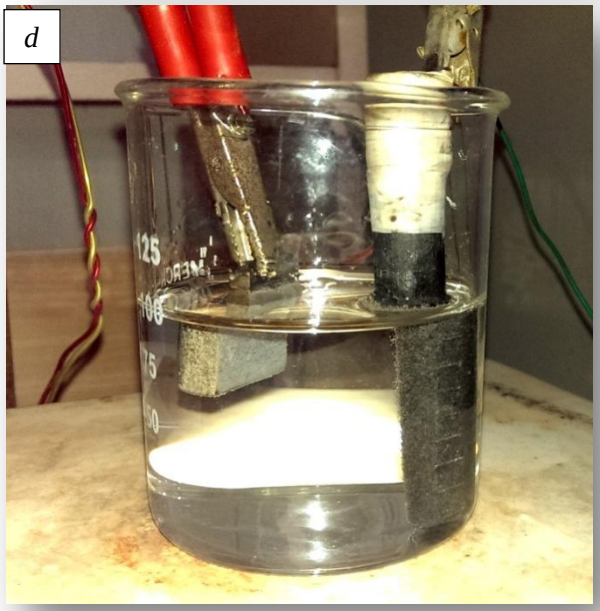
b



c


150 ml

d



e

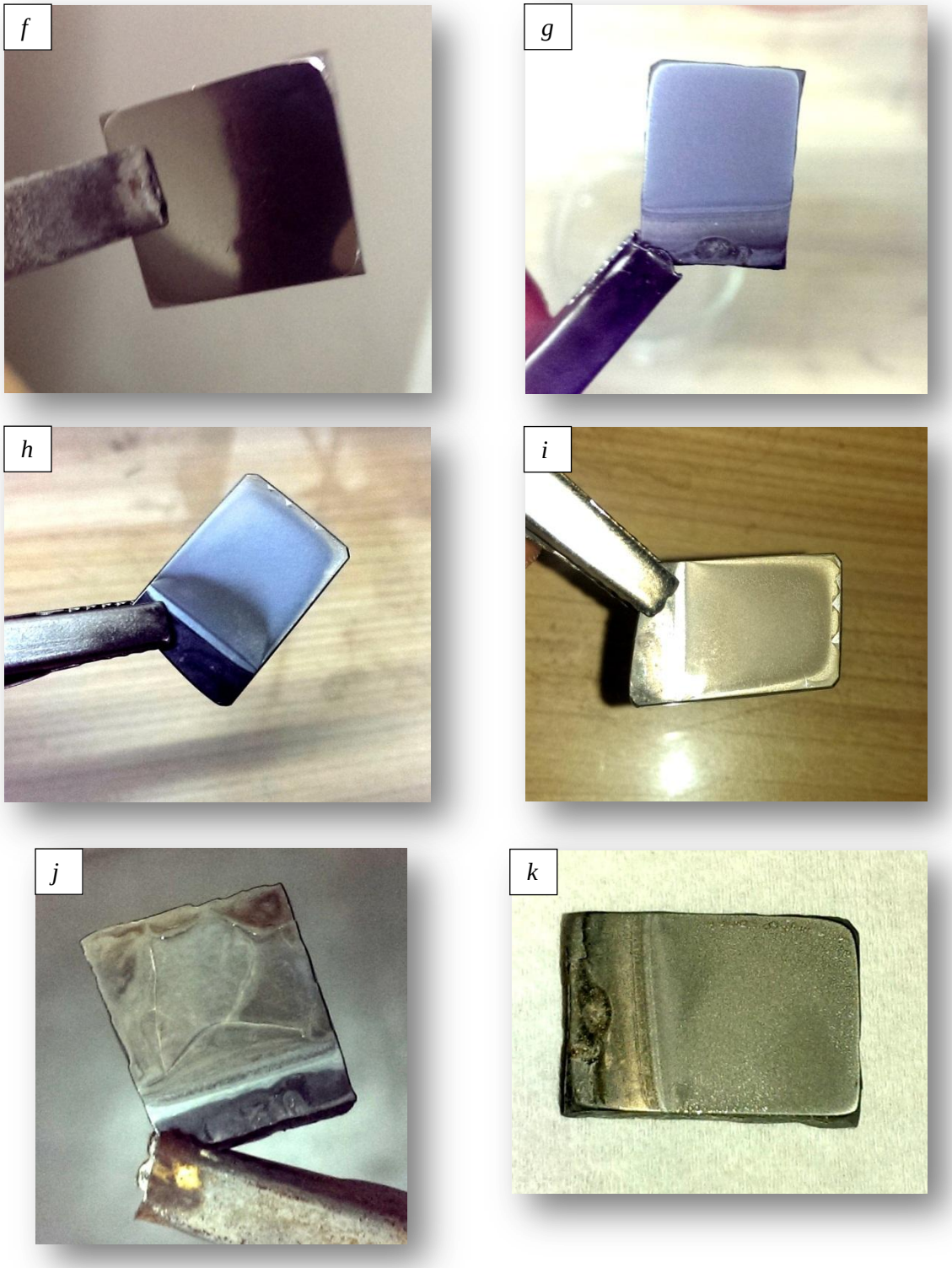


Fig.3.2 (a) Experimental Setup, (b)Ti6Al4V sample taken as anode and graphite as cathode, (c)Electrode system fixed inside the electrolyte, (d) Ti6Al4V Sample undergoing anodization, (e)Anodized Ti6Al4V sample, (f)Polished sample before anodization, (g, h, i, j)Different samples after anodization by varying process parameters, (k)Anodized sample washed in ethanol and then dried.

Table 3.1 Different Electrolyte solutions used for producing Titania nano-tubular structures

Sample No.	Electrolytes	Duration (hrs.)	Voltage (V)	Ref.
1	0.5%HF	1	10	44
2	0.5%HF	1	20	
3	1.5% HF	1	10	43
4	1.5%HF	1	20	
7	1M H_2SO_4/0.15%HF	1	30	45
8	1M H_2SO_4/0.15%HF	4	30	
5	CH_3COOH/0.5M HF	4	10	41
6	CH_3COOH /0.5M HF	4	15	
9	CH_3COOH /0.5M HF	4	20	
10	CH_3COOH /0.5M HF	4	25	
11	CH_3COOH /0.5M HF	4	30	
12	CH_3COOH /0.5M HF	6	10	
13	CH_3COOH /0.5M HF	6	15	
14	CH_3COOH /0.5M HF	6	20	
15	CH_3COOH /0.5M HF	6	25	
16	CH_3COOH /0.5M HF	6	30	

3.4 Characterization of the samples

3.4.1 Morphology Analysis

For microstructural study: Optical microscope from ZEISS with the facility of digital image recording system has been used. The prepared sample was placed on the horizontal stage with the surface perpendicular to the optical axis of the microscope and illuminated through the objective lens by light from a lamp or arc source. This light was focused by the condenser lens into a beam that is made approximately parallel to the optical axis of the microscope by a half-silvered mirror. The light then passes through the objective onto the specimen. It was then reflected from the surface of the specimen, back through the objective, the half-silvered mirror, and then to the eyepiece to the observer's eye, or to a camera port or a film plane. All the images were captured at

500X magnification. A comparative study of microstructures of the as received Ti6Al4V specimen as well as various electrochemically treated Ti6Al4V has been carried out in the next chapter.

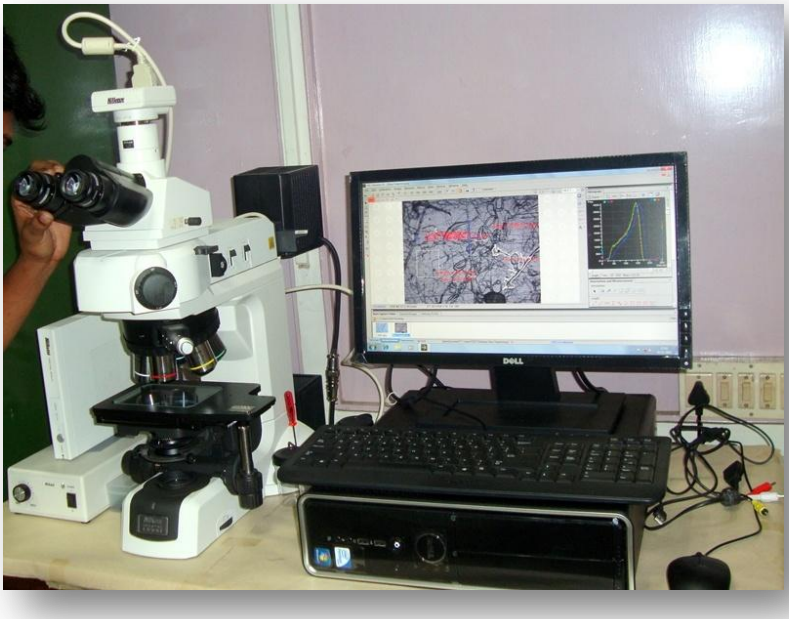


Fig.3.3 Metallurgical Binocular Compound Microscope equipped with digital image recording system.

3.4.2 Phase Analysis (XRD)

For phase exploration: The composition of the pure Ti6Al4V and anodically oxidized samples was analyzed using X-Ray diffraction. Samples were studied using X'PERT PANalytical X-Ray Diffractometer. A Cu target was used as X-Ray source (CuK-radiation). X-Ray intensity was measured for angles (2θ) in the range 30°-80° with scan rate of 2° per minute. The diffraction patterns produced were then compared with the existing data using JCPDS data file. To identify the phases present, the location of peaks in the XRD profiles were compared to reference spectra. Qualitative analysis of α & β phase of titanium and rutile & anatase phase of TiO_2 has been done by using reference database 44-1294, 44-1288, 73-1765 and 84-1286 respectively. A detailed study of the peaks obtained has been done in forthcoming chapter.

Fig.3.4 XRD Machine for phase characterization Model No. - X` Pert, 3040/00Company- PAN Analytical

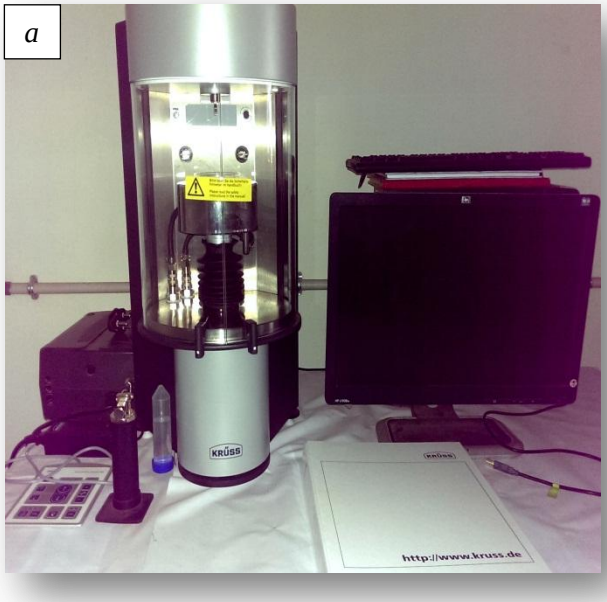
3.4.3 Micro-hardness Test

For hardness evaluation: Microhardness of the non-oxidized and oxidized Ti6Al4V samples were determined by using LECO microhardness tester (*Fig.3.6.4.3*). The machine was equipped with minimum 1gf and maximum 1000gf load. Initially before testing, the vertical lines seen through the eyepiece was calibrated. The vertical lines were adjusted such that their edges were adjacent to each other. The *reset* button was pressed and then the sample was placed on the horizontal platform for indentation. The test was carried out with 300gf load with dwelling time 10 seconds to ensure that the indentation was up to the oxidized surface. For each sample, three different locations were indented and their hardness was recorded. These values were then averaged to get the overall hardness of the oxidized surface.

Fig.3.5 LECO Microhardness Tester for measuring Vickers Hardness.
Model No.-LM248AT
Company- LECO Corporation, Michigan, USA.

3.4.4 Wettability Test

For wettability analysis: With the aim of inspecting the wetting characteristics & surface energy of the treated and untreated specimens of Ti6Al4V alloy, the contact angle of the samples were evaluated using distil water. The contact angle between the as received and the oxidized samples were calculated and compared by two methods: Tensiometer and Sessile drop method. The surface energy was evaluated using the software provided in the Tensiometer. In droplet method, the contact angle measurement was performed by a setup consisting of a specially designed clamp, syringe and high resolution digital camera. The syringe was filled with distil water and fixed properly on the clamp with an approximate distance of 2mm between the needle-tip and the sample surface. The plunger was pressed very slowly and gently so as to get a single drop of water of diameter nearly 0.5mm over the surface of the specimen. The image of the poured drop was taken with the help of a 12MP digital camera. With the help of ImageJ software, contact angle between the solid, liquid and gas interface was measured from the image.



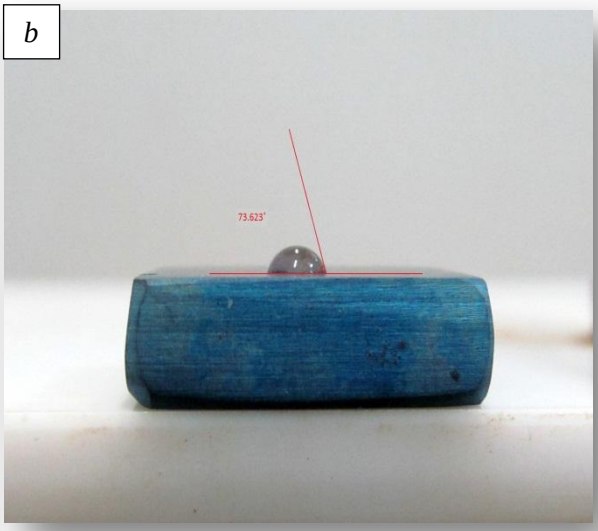


Fig.3.6 Two methods of measuring contact angle:
(a)Tensiometer
Model-K100//3000289
Company-KRUSS GmbH Germany

(b) Sessile Drop Method
Camera Model- PowerShot SX150 IS
Company- Canon

CHAPTER 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSIONS

Anodic oxidation of Ti6Al4V has been carried out in different electrolytes to develop a nano-structure TiO_2 surface. The effect of voltage and time duration has been studied to see its effect on the formation of oxide layer. The detailed morphology, phase purity, hardness and surface properties of the newly formed oxide surface are discussed in the present section.

4.1 Morphology Analysis

4.1.1 *Effect of electrolyte on oxide formation in Ti6Al4V surface at 10V for 1hr.*

The first set of study was conducted to analyze the effect of various electrolytes, on oxide layer formation of Ti6Al4V surface. *Fig 4.1(a-d)* represents the same in the form of optical micrographs.

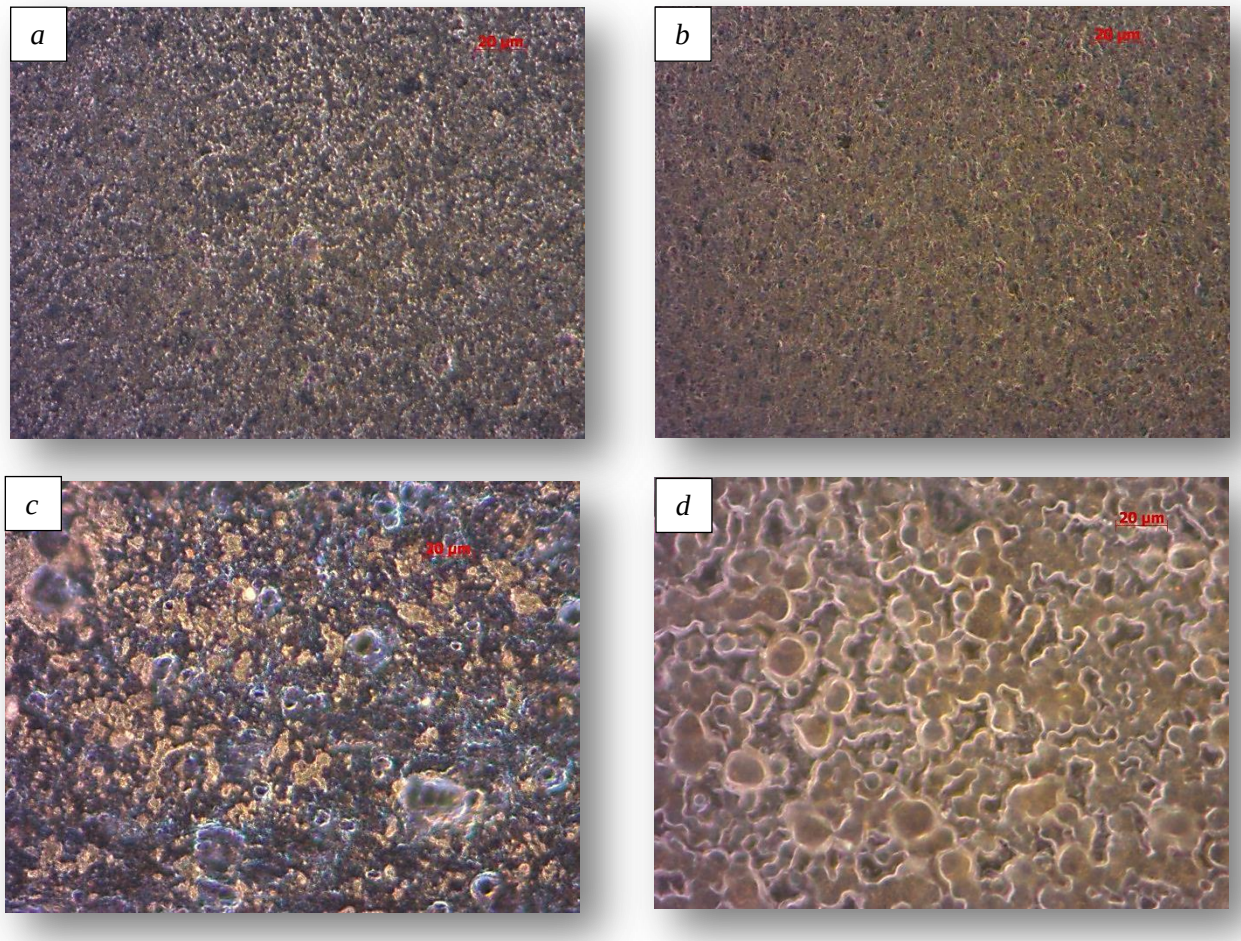
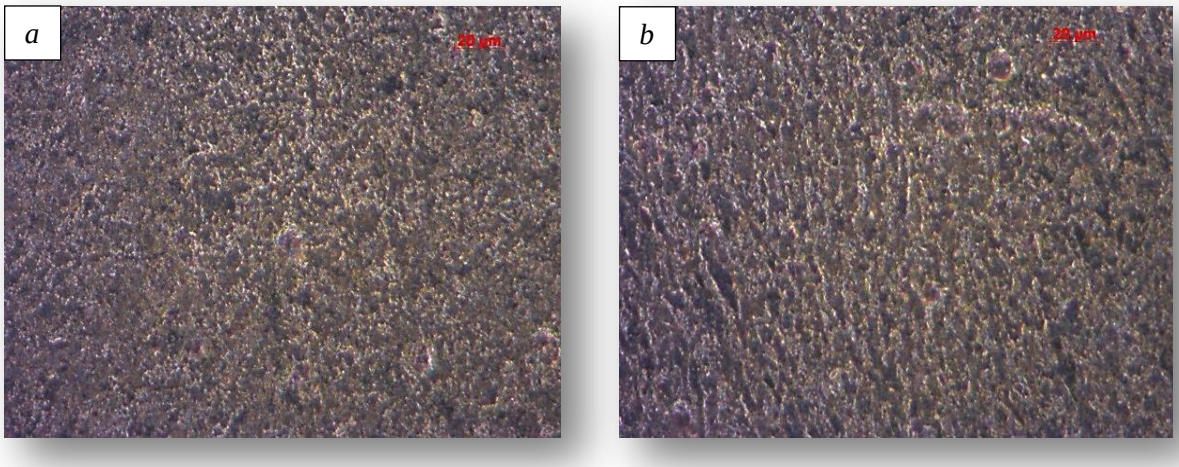


Fig4.1 Microstructure of the samples as seen under optical microscope, when oxidized in (a) 0.5% HF (b) 1.5% HF (c) 1M H_2SO_4/0.5%HF (d) CH_3COOH/0.5M HF

The mirror finished surface of untreated substrates generally shows a steel grey color. However, in the present case most of the modified surfaces exhibit a dark brown color. This transformation can be attributed to the formation of oxide layer over the non-oxidized Ti6Al4V surface *Fig.4.1 (a)* Suggests an electrolytic treatment with HF concentration of 0.5% for 1hr at 10V. The deep brown, closely packed oxide layer was formed uniformly all over the surface. The porous spots were evenly distributed throughout the viewed field. *Fig.4.2 (b)* shows a micrograph similar to *Fig. (a).* Nonetheless, the packing of oxide layer was slightly denser. *Fig.4.1 (c)* depicts the surface of anodically oxidized Ti6Al4V surfaces with 1M H_2SO_4/0.15% HF solution. The formation of distinct, small black spots, evenly distributed all over the surface, was observed. These black spots were circular but the sizes of these spots were highly diverse. *Fig.4.1 (d)* suggests the formation of non-uniform, micro-sized globular structures which are lined with bright edges. Few globules also indicate the presence of a dark circular spot at the center. The dimension of the black spot shows a wide range of variation and their distribution is highly uneven.

4.1.2 Effect of voltage on oxide formation on Ti6Al4V surface for 1hr.

To study the effect of the process parameters more precisely, oxidation of samples was carried out at two different voltages, for each electrolytic solution.



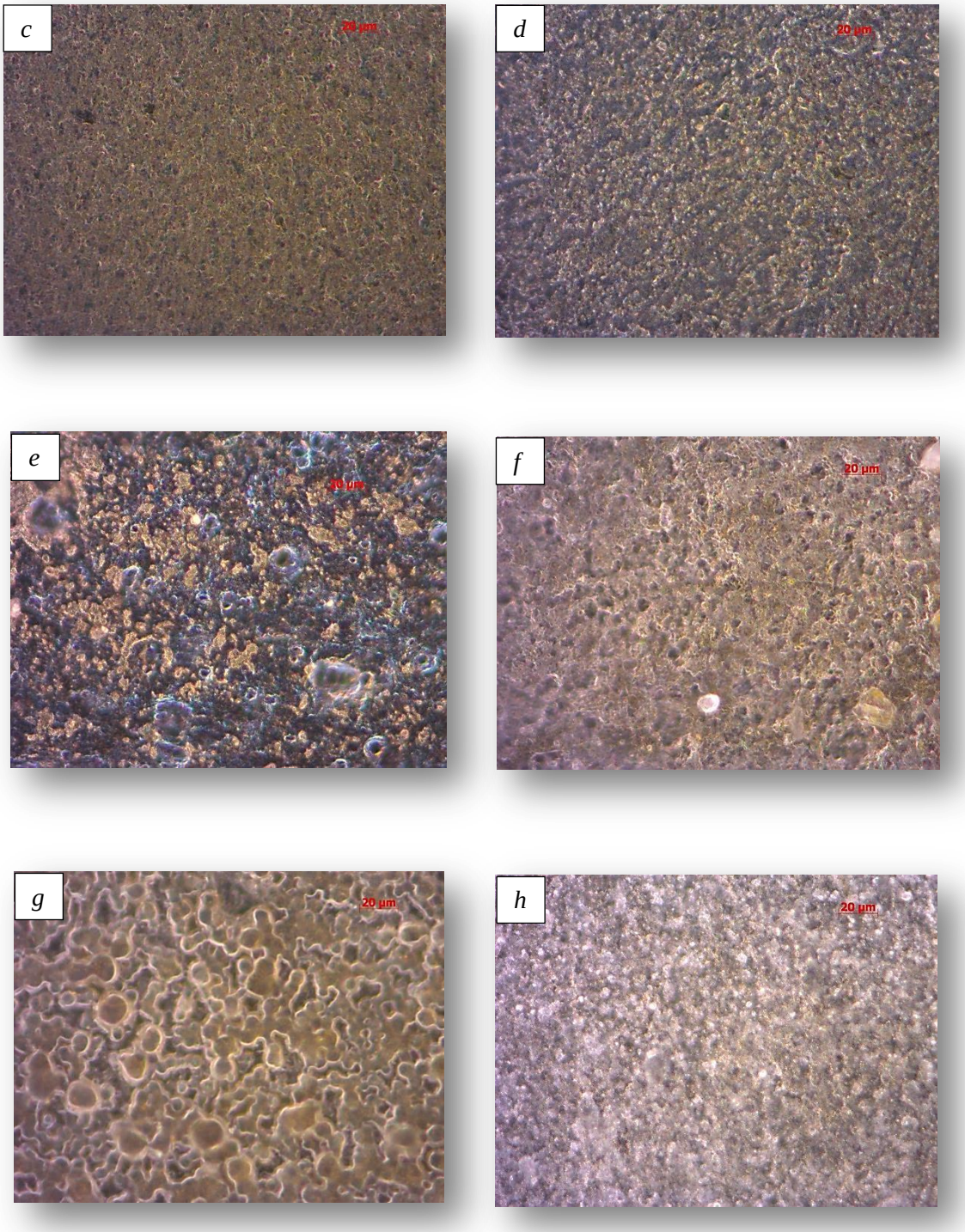


Fig. 4.2 Microstructure of the samples as seen under optical microscope, when oxidized in (a) 0.5% HF, 10V (b) 0.5% HF, 20V (c) 1.5% HF, 10V (d) 1.5% HF, 20V (e) 1M H_2SO_4/0.5%HF, 10V (f) 1M H_2SO_4/0.5%HF, 20V (g) CH_3COOH/0.5M HF,10V (h) CH_3COOH/0.5M HF,20V

Fig.4.2 (a) & (b) depicts the treatment of samples in 0.5% HF at 10 V and 20V respectively. Although a very trivial difference in pore size could be observed, yet no significant increase was present at a higher voltage.

Fig.4.2 (c) & (d) represents the use of 1.5% HF as buffer media at 10V and 20V. At higher voltage, the oxide layer appears more grain like. Both, pore density and size seem enhanced at 20V.

Fig.4.2 (e) & (f) demonstrate the anodization of Ti alloy with 1M H_2SO_4/0.5%HF using two different voltages (10V & 20V). At 10V distinct pore like structures were observed but their sizes were visibly variable. On supplying a voltage of 20V the pores showed an even distribution and uniform size all over the surface.

It could be suggested from *Fig.4.2 (g)* that on using a combination of CH_3COOH/0.5M HF at 10V the process of pore formation was promoted and globular structures with roughly pore like morphology were formed at the center. The morphology further improved on using voltage of 20V. *Fig.4.2 (h)* depicts the formation of uniformly distributed circular grains. The micro-graph indicates the presence of distinct dark spots in some regions. However, a nano-scale magnification is essential to confirm the formation of pores/tubes.

From the comparison of the two process parameters, it could be deduced that the treatment using a combination of CH_3COOH/0.5HF at 20V produced the finest results. Therefore it was selected for further optimization.

4.1.3 Effect of time on oxide formation on Ti6Al4V surface when anodized in CH_3COOH/0.5HF at 20V

Anodic oxidation of Ti6Al4V samples were carried out for four different lengths of time i.e. 1, 2, 4 and 6 hours *(Fig.4.3 (a), (b), (c), (d))* respectively, to study the effect of treatment time on the morphology of the oxide layer.

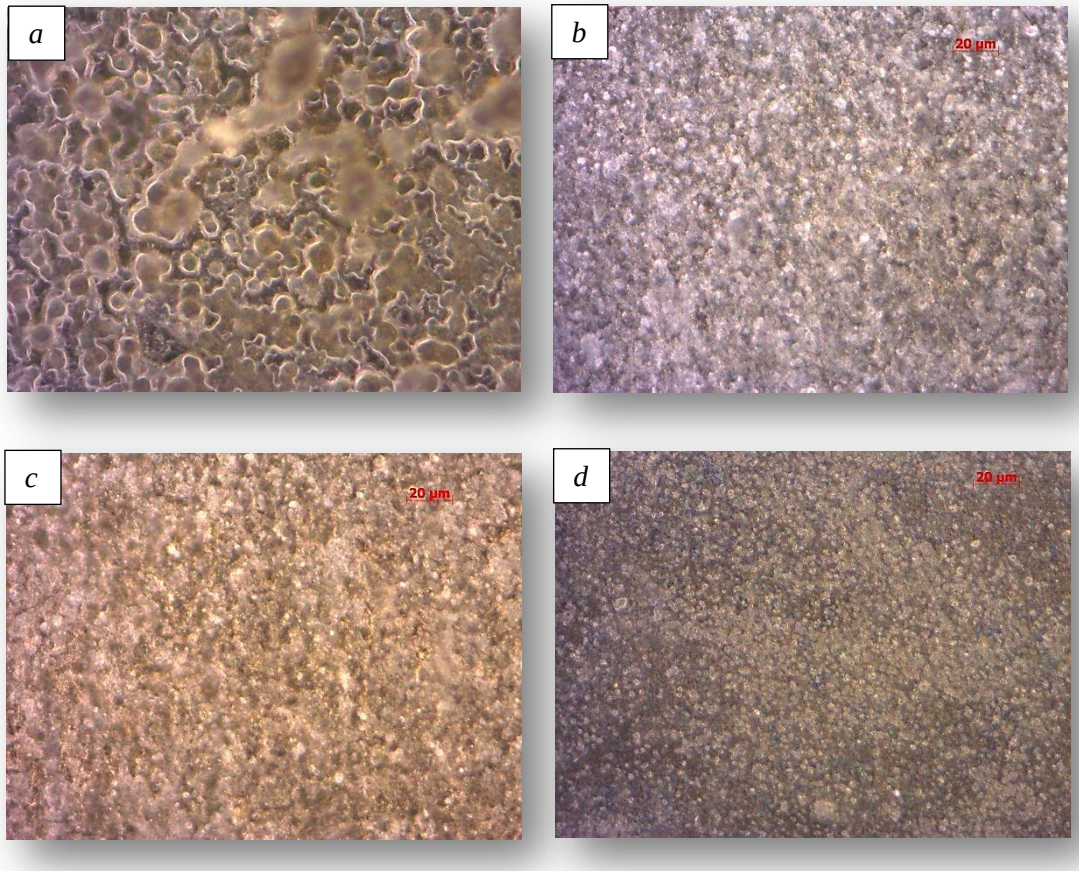


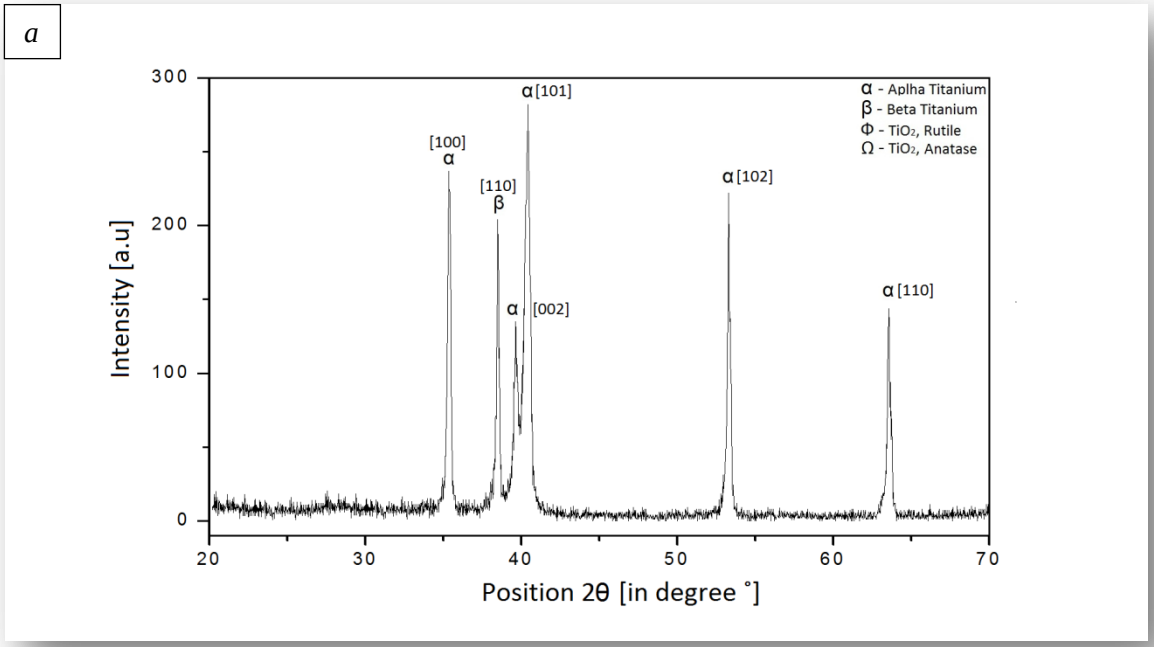
Fig. 4.3 Microstructure of the samples as seen under optical microscope, when oxidized for (a) 1hr (b) 2hrs (c) 4hrs (d) 6hrs

It is evident, that the self-assembly process initiated within the treatment time of 1 hr. However, the pores were not well organized, scarce and randomly dispersed over the surface *Fig.4.3 (a).* The samples with treatment time of 2 and 4 hours respectively, depict a more organized morphology with a rise in the number of pores *Fig.4.3 (b), (c).* It also shows the presence of another 'hole' like structure along with the pores. At 6hrs, it was observed that the porous structures formed on the surface were completely organized and evenly scattered all over. Moreover, most of the porous structures appeared similar in morphology. These observations can be backed by the Ref [45] that explained the formation of the nanostructures with the passage of time. Initially, pores begin to form due to dissolution of the oxide layer at the weak points. Later, another pore like structures appears at the inter-pore regions and is known as void. After a longer treatment time, both pores and voids grow deeper and give rise to the final porous surface.

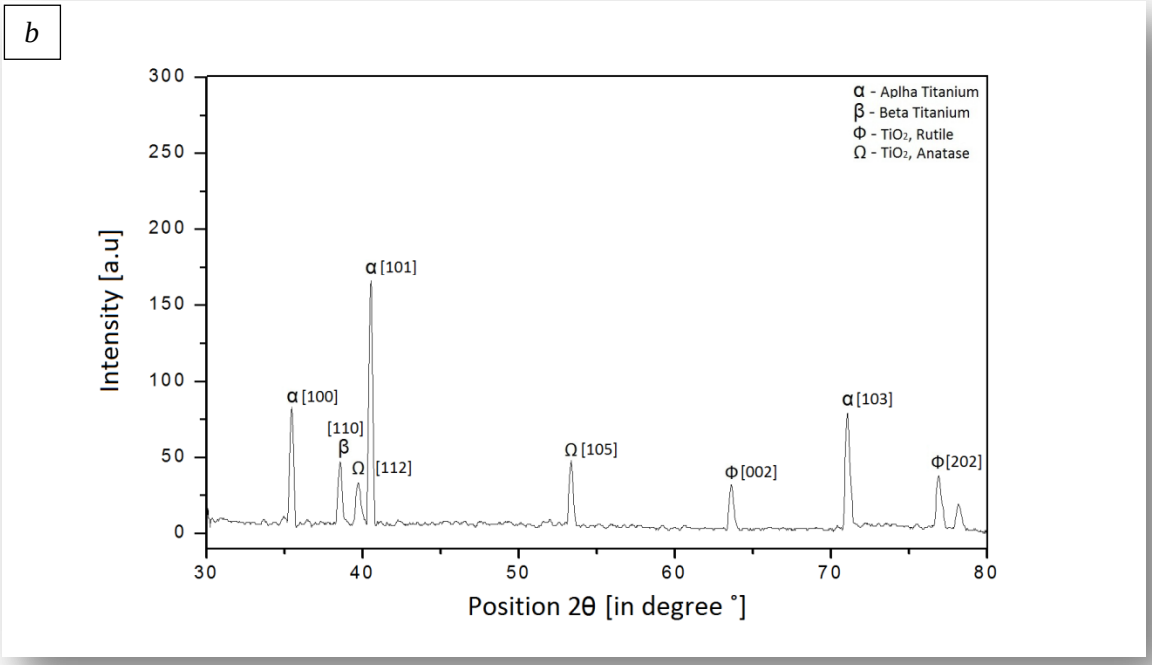
4.2 Phase Analysis (X-Ray Diffraction)

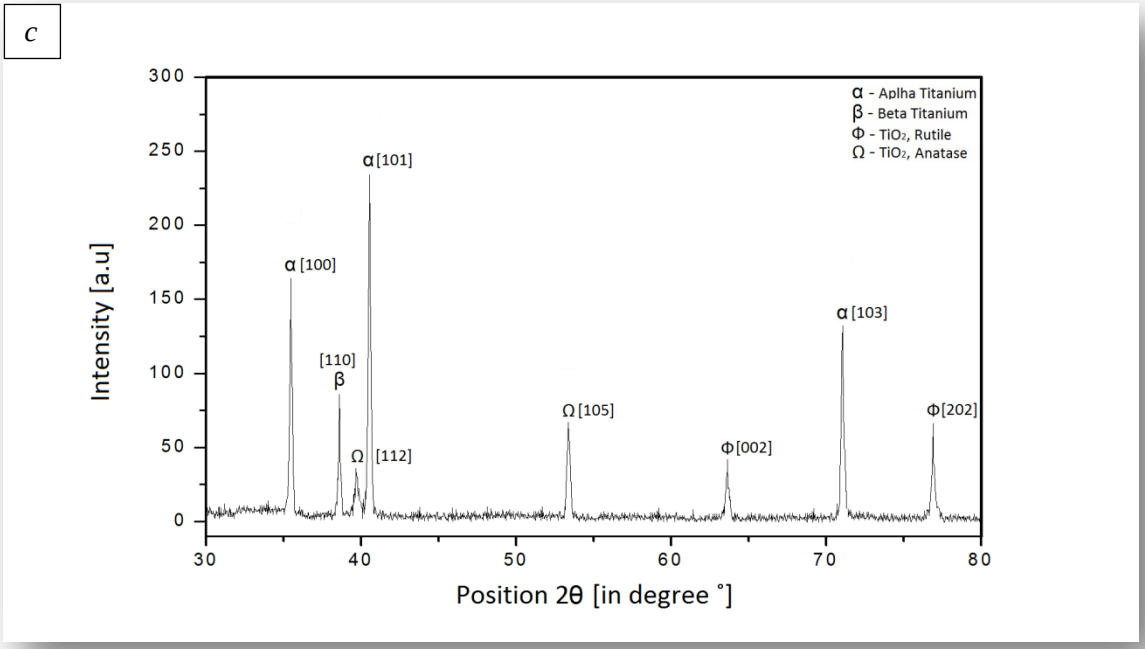
The influence of the electrochemical treatment on the crystalline structure of the oxide produced by the anodic oxidation process was measured with XRD. Obtained peaks were matched with JCPDS data card no. **84-1286** (TiO_2, Anatase, syn), **73-1765** (TiO_2, Rutile, syn), **44-1294** (αTi) and **44-1288** (β Ti).

a



b





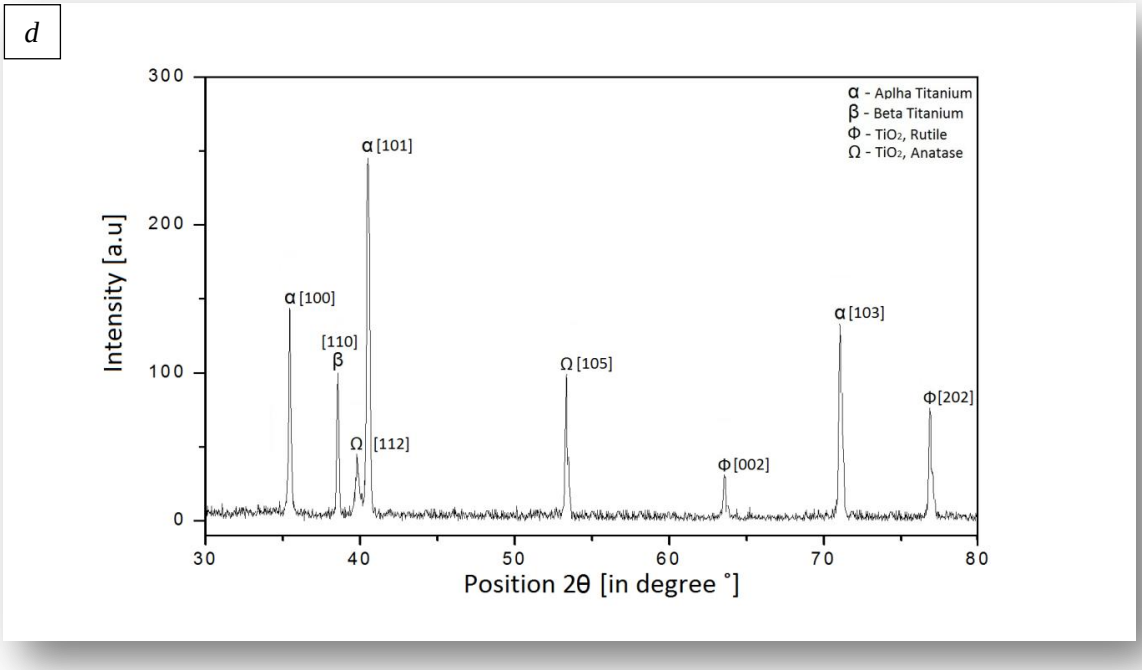


Fig. 4.4 XRD pattern of different Ti6Al4V specimens:

(a) Non-oxidized pure and polished Ti6Al4V sample.

(b) Anodized Ti6Al4V sample in CH_3COOH /05 M HF at 20V for 2hrs.

(c) Anodized Ti6Al4V sample in CH_3COOH /05 M HF at 20V for 4hrs.

(d) Anodized Ti6Al4V sample in CH_3COOH /05 M HF at 20V for 6hrs.

Fig.4.4 represents the XRD profiles of the non-oxidized polished Ti6Al4V substrate as well as the Ti6Al4V substrates which have been anodized in acetic acid medium at 20V for 2hrs, 4hrs and 6hrs respectively. The XRD patterns of untreated Ti6Al4V alloy are represented in *Fig.4.4 (a).* Untreated Ti6Al4V alloy comprises of α + β phase (denoted as 'α' Ti and 'β'Ti) in the figure. The XRD patterns of electrochemically oxidized Ti6Al4V alloy samples indicate the presence of anatase and small amount of rutile along with α & β titanium peaks. At different diffraction angles, peaks for both the phase of titanium i.e. α-Ti and β-Ti, have been observed to match with the different crystallographic planes of non-treated sample *(Fig.4.2 (a)).* It is clearly visible from the peaks that the quantity and intensity of α-Ti outnumbers β-Ti peaks. Hence it can be concluded that the untreated Ti6Al4V comprised of titanium mainly in α-Ti phase with small amount of β phase. The peaks obtained after oxidation for the rest of the three processing parameters *(Fig.4.2 (b, c, d))* indicate the presences of all the phases i.e. anatase, rutile phase of TiO_2 and α-Ti, β-Ti phase of Ti. Moreover, the locations of α-Ti peaks appear to be preserved while the emergence of rutile peak is observed at higher angles. The only difference which came into existence is the appearance of the same peak at slightly different angle locations for the four samples. This can be attributed to the shifting of the peak locations due to non-ideal conditions of the Ti6Al4V samples used for this study. The Ti sheet used was cold-pressed & rolled and therefore a residual compressive stress exists within the crystal lattice of the Ti sheet. This compressive stress results in lowering of the distance between two consecutive planes within the crystal arrangement. For a constructive interference of diffracted x-rays to takes place, it must satisfy the Bragg's law condition [49].

$$n\lambda = 2d\sin\theta$$

Where, n is any integer,

λ is the wavelength of X-ray,

d is spacing between the planes in the atomic lattice,

θ is the angle between the incident ray and the scattering planes.

Considering nλ as constant during XRD, the term 1/d varies with the variable sinθ. Therefore, as d is inversely proportional to θ, a consequent decrease in d-spacing results in increase of the diffraction angle where the peaks are produced. As a result, a shifted peak is observed when compared with the standard database.

In a nutshell, the presence of anatase in the oxidized layer in large amount is expected to affect the wettability and hardness of the surface as anatase, in its physical form, is more wettable and harder than the substrate itself.

4.3 Microhardness Analysis

The microhardness of the various anodized specimen was evaluated using a Vickers microhardness tester. All the tests were carried out at a load of 300gf with dwelling time 10 seconds. Table 4.1 shows the Vickers hardness values of the Ti6Al4V specimen that were anodized in CH_3COOH at 20V for 1hr, 2hrs, 4hrs and 6hrs time duration.

Table 4.1 Microhardness of the Ti6Al4V specimen anodized in CH_3COOH at 20V.

Sample No.	HV (gf/μm^2)
As received	334.4±10
1hr	387.7±10
2hrs	447.8±10
4hrs	556.5±10
6hrs	615.3±10

Table 4.2 Microhardness of the Ti6Al4V specimen anodized in CH_3COOH 6hrs.

Sample No.	HV (gf/μm^2)
As received	334.4±10
10V	600.4±10
20V	615.3±10

The hardness of the non-oxidized Ti6Al4V sample was found out to be 334.4 HV. It can be observed from the table that there is a remarkable increase in surface hardness of the Ti6Al4V samples that were subjected to oxidation. The hardness increased with the increase in time of anodization. As the time duration of oxidation increases, more number of Ti atoms is oxidized to TiO_2. Since major of the oxides of titanium that are formed in anatase phase (from XRD), the overall hardness of the sample is expected to increase. The hardness of pure TiO_2 in anatase phase

is VHN_{100}=616 - 698 kg/mm^2 [50]. As the XRD data confirms the presence of TiO_2 on the surface of anodized samples, the obtained hardness values confirms our expected result. Since majority of the oxide layer formed are in anatase phase, the rise in values hardness can be attributed to the consequence increase in anatase formation. In other words, the hardness of oxidized Ti6Al4V substrate increases with the increase in time duration of anodization.

4.4 Wettability Analysis

The surface property of a material such as wettability can be analyzed by evaluating the contact angle between its surface and a liquid medium. The wettability test of the treated and untreated Ti6Al4V alloy samples have been carried out using distil water. Table 4.3 shows the different contact angle values obtained by the Sessile drop method.

Table 4.3 Contact angle of the Ti6Al4V specimen anodized in CH_3COOH at 20V, measured by Sessile drop method.

Sample No.	Contact Angle(°)
As received	74.889
1hr	59.02
2hrs	59.79
3hrs	60.35
4hrs	57.72

(*Fig.4.3*) shows the image of the contact angle of an oxidized and a non-oxidized sample measured by the sessile drop method. When any material is implanted into the body, it first comes in contact with the protein-rich liquid phase which is nearly aqueous in nature. This brings on a rearrangement of proteins on the surface of the material accompanied by cell attachment. In order to assess this situation, the wetting test of material surface is assumed to be the predictive index of cyto-compatibility [51]. The contact angle for the bare Ti6Al4V was found out to be 74.889°. When the Ti6Al4V samples were oxidized electrochemically, there seemed to be a decrease in the contact angle of the treated surfaces. The fall in contact angle indicates that the oxidized layers so formed are hydrophilic in nature. It has been seen that the oxygen content of a material's surface prove to be a significant factor in controlling the wetting activity of the material [52]. The surface

oxygen content rises with wettability and reveals that the rise in the surface oxygen content is accountable to some extent for the general rise in the wettability characteristics [53-54].

4.5 Surface Energy Analysis

The data in the Table 4.4 showcases the different values of contact angle and free surface energy obtained for the same samples using a Tensiometer.

Table 4.4 Contact angle & surface energy of the Ti6Al4V specimen anodized in CH_3COOH at 20V, measured by Tensiometer.

Sample No.	Contact Angle (°)	Surface free Energy (mN/m)
As received	75.33	35.5
1hr	60.22	47.7
2hrs	58.79	48.6
3hrs	59.4	48.2
4hrs	57.46	49.4

The data indicates that the free surface energy of the treated sample is remarkably higher than the untreated sample. The above two important results strongly suggest that the modified surface is hydrophilic in nature. This implies that the adhesion of live human cells is more likely to happen on the treated samples with much ease and lesser time than the untreated one.

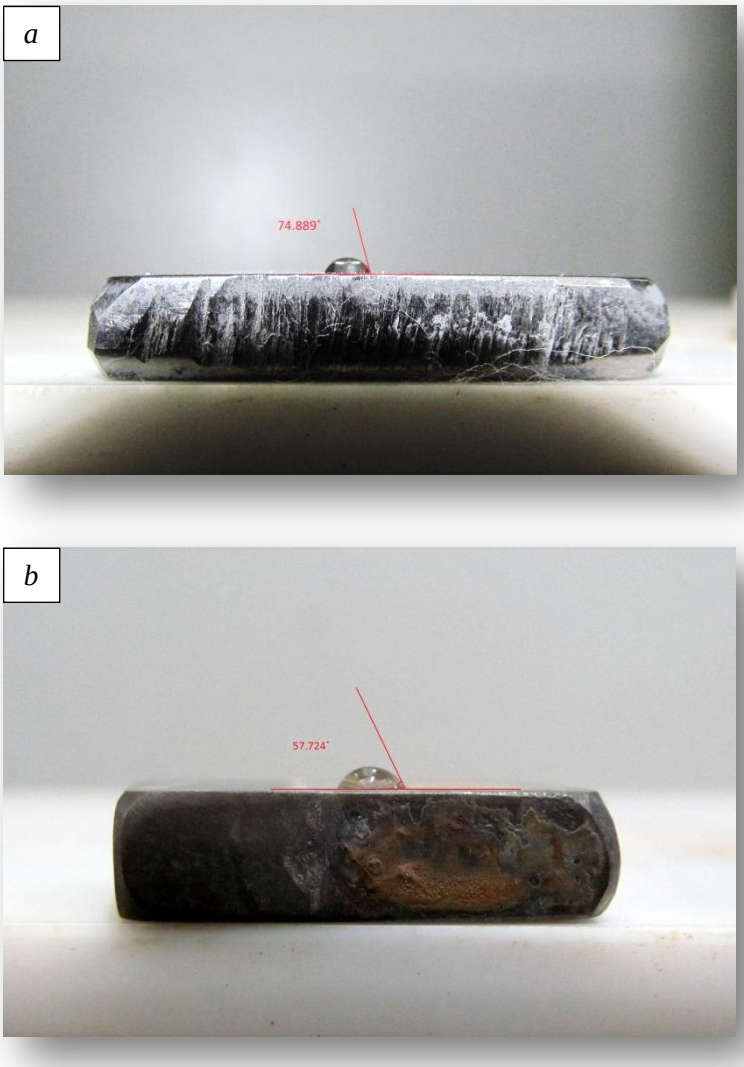


Fig. 4.5 Contact angle of (a) pure and polished Ti6Al4V sample (b) an anodized Ti6Al4V sample.

CHAPTER 5

CONCLUSION

&

FUTURE SCOPE

CONCLUSION & FUTURE SCOPE

On performing anodization of Ti6Al4V samples in the four different types of electrolytes (refer Table no. 3.1), i.e 0.5M HF in CH_3COOH, 0.5% HF, 1.5% HF and 0.15% HF in 1M H_2SO_4, various types of surface morphology was observed. Surface polishing was a crucial step before anodization as it gave a mirror-like smooth surface. This helped in a better and uniform oxide layer formation. An early inspection of the anodized samples using optical microscope revealed that the microstructure morphology of the samples anodized in acetic acid medium appeared to be more dense and uniform. Therefore, CH_3COOH/0.5M was optimized as the electrolyte and was used for experimenting on other Ti6Al4V samples by varying the process parameters, i.e. time duration and voltage.

Usually, titanium dioxide can exist in three crystalline forms, in which the anatase and rutile phases are more useful than the brookite phase. The XRD data confirmed the presence of anatase and rutile form of TiO_2 in the oxidized layer obtained by anodization. The micro-hardness results also confirmed that hardness of the oxidized substrate was highest for the sample which was oxidized for the maximum duration of time. The wettability studies confirmed the hydrophilic nature of the oxide surface. This wettability and surface energy results obtained imply a very import and advantageous aspect in terms of better cell growth and adhesion. Therefore the objective of obtaining a better surface chemistry and microstructure than native oxide layer was achieved. Micro-structured titanium dioxide coating has an immense potential for enhanced biological response in various biomedical applications such as improvement in surface interaction biocompatible implants with surrounding tissues [55]. As a further application of anodic oxidation of Ti6Al4V, a higher voltage condition can be provided so that nano-tubular structures are formed with much ease and convenience. Titania nanotubes are of great significance in the field of biomedical science, drug delivery, photo catalytic activities and biosensor devices.

CHAPTER 6

REFERENCES

REFERENCES

[1] Kovacs. P. and Davidson J.A., *Chemical and electrochemical aspects of the biocompatibility of titanium and its alloys*. In: Brown S.A. and Lemons J.E., Editors, Medical Applications of Titanium and its Alloys: The Materials and Biological Issues (1996) ASTM STP 1272, p. 163.

[2] Hunt J.A. and Stoichet M., Curr. Opin. *Solid State Mater*. Sci. **5** (2001), p. 161.

[3] Williams D.F., *Titanium and titanium alloys*. **vol. II**, CRC Press (1981), p. 9.

[4] Long M.J. and Rack H.J., *Biomaterials* **19** (1998), p. 1621.

[5] Perl D.P. and Brody A.R., *Science* **208** (1980), p. 297.

[6] Crapper D.R., McLachlan D.R., Farnell B., Galin H., Karlik S, Eichhorn G. and Deoni U., *Aluminum in human brain disease*, Raven Press, New York (1993), p. 209.

[7] Sittig C., Textor M., Spencer N.D., Wieland M. and Vallotton P.H., J. Mater. Sci. Mater. Med. **10** (1) (1999), p. 35.

[8] Wen H.B., Wolke J.G., Wijn J.R., Liu Q., Cui F.Z and de Groot K., *Biomaterials* **18** (1997), p. 1471.

[9] Nie X., Leyland A. and Matthews A., Surf. Coat. Technol. **149** (2002), p. 245.

[10] Brendel T., Engel A. and Russel C., J. Mater. Sci. Mater. Med. **3** (3) (1992), p. 175.

[11] Andreazza P., De Barros M.I., Andreazza-Vignolle C., Rats D. and Vandenbulcke L., ThinSolidFilms **319** (1998), p. 62.

[12] Uchida M., Nihira N., Mitsuo A., Toyoda K., Kubota K. and Aizawa T., Surf. Coat. Technol. 177–178 (2004), p. 627.

[13] Kweh S.W.K, Khor K.A. and Cheang P., Biomaterials **23** (3) (2002), p. 775.

[14] Hanawa T., Kamiura Y., Yamamoto S., Kohgo T., Amemiya A., Ukai H., Murakami K. and Asaoka K., J. Biomed. Mater. Res. **36** (1997), p. 131.

[15] Guleryuz H. and Cimenoglu H., Biomaterials **25** (2004), p. 3325.

[16] Biomaterials, lecture14BME 551 / 551EPE2009.

[17] J. Choi, R. B. wehrspohn, J. Lee, U. Gosele, Electrochimica Acta 49, p.2645

[18] Pilliar R.M., and Weatherly G.C. (1984). Developments in Implant Alloys,CRCCrit. Rev.Biocompatibility, **1**: 371-403..

[19] Dong H. and Bell T., Enhanced wear resistance of titanium surfaces by a new thermal oxidation treatment, Wear**238** (2000), pp. 131–137.

[20] Bloyce A., Qi P.Y., Dong H. and Bell T., Surface modification of titanium alloys for combined improvements in corrosion and wear resistance, SurfCoatTechnol**107** (1998), pp. 125–132.

[21] Wadewitz V, Breme J. TiTa-Legierungen für dentale Implantate—Korrosionsverhalten, einschließlich Kontaktkorrosion. Z Zahnärztl Implant 1989;**5**(2):116–120.

[22] Kurella, Kumar A., "Laser Induced Hierarchical Coatings on Titanium Alloy. " PhD diss., University of Tennessee, 2009.

[23] Tan,J. and Saltzman,W.M.(2004). Biomaterials with hierarchically defined micro- and nanoscale structure, Biomaterials**,25:** 3593-3601.

[24] Boyer R.R, Lutjering G, Proceedings of Advances in the Science and Technology of Titanium Alloy Processing, Anaheim, CA, USA (1996) 349

[25] Liu et al. Surface modification of titanium, titanium alloys,and related materials for biomedical applications / Materials Science and Engineering R 47 (2004) 49–121

[26] Structural Alloys Handbook, Battelle's Columbus Laboratories,Columbus, OH, (1982).

[27] Bloyce A., Morton P., Bell T., ASM Handbook, vol. 5, ASM International, Materials Park, OH, (1994) 835.

[28] Sittig C., Textor M., Spencer N.D., Wieland M., Vallotton P.H., J. Mater. Sci. Mater. Med. 10 (1) (1999) 35

[29] Taborelli M., Jobin M., Francois P., P. Tonetti, S. Szmukler-Mocler, J. P. Simpson, P. Descouts, Clin. Oral Implants Res. 8 (3) (1997) 208.

[30] Wen H.B., Wolke J.G., Wijn J.R., Liu Q., Cui F.Z., de Groot K., Biomaterials 18 (1997) 1471.

[31] D. Gong, C. A. Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen, and

[32] Wen H.B., Liu Q., Wijn J.R., de Groot K., J. Mater. Sci. Mater. Med. 9 (1998) 121.

[33] G. K. Mor, O. K. Varghese, M. Paulose, N. Mukherjee and C. A. Grimesa,

[34] Xiao F, Tsuru K., Hayakawa S., Osaka A., Thin Solid Films 441 (2003) 271–276.
R. Beranek, H. Hildebrand, and P. Schmuki, Electrochemical and solid-state

[35] Afshar, Vaezi M.R., Surface & Coatings Technology 186 (2004) 398– 404.

[36] Ghicov A., Tsuchiya H., Jan M. Macak, P. Schmuki, Electrochemistry Communications 7 (2005) 505–509.

[37] Baszkiewicz J., Vacuum 78 (2005) 143–147.

[38] Rie K.T, Stucky T., Silva R.A., E. Leitao, Surf. Coat. Technol. 74– 75 (1995) 973.

[39] Bell T., Bergman W., Lanagan J., Morton P.H., Staines A.M., Surf. Eng. 2 (1986) 133.

[40] Yilbas B.S., Sahin A.Z., Al-Garni A.Z., Said S.A.M., Ahmed Z., Abdulaleem B.J., Sami M., Surf. Coat. Technol. 80 (1996) 287.

[41] da Silva S. L.R., Kerber L.O., Amaral L., dos Santos C.A., Surf. Coat. Technol. 116–119 (1999) 342.

[42] Gokul Lakshmi D. Arivuoli D., Ganguli B., Mater. Chem. Phys. 76 (2002) 187.

[43] Fleszar A., T. Wierzchon T., Sun Kyu Kim, J. R. Sobiecki J.R., Surf. Coat. Technol. 131 (2000) 62.

[44] Wierzchon T., Fleszar A., Surf. Coat. Technol. 96 (1997) 205.

[45] Renevier N., Collignon P., Michel H., Czerwiec T., Surf. Coat. Technol. 111 (1999) 128

[46] Coll B., Pellman M., Souchard, Jacquot P., Proceedings of Surface Modification

[47] Siva Rama Krishna D., Brama Y.L. and Sun Y., Tribol. **40** (2007)

[48] Guleryuz H.and Cimenoglu H., Biomaterials **25** (2004), p. 3325.

[49] Kumar Satendra, Sankara Narayanan T.S.N. , Ganesh Sundara Raman S.and Seshadri S.K., *IThermal oxidation of Ti6Al4V alloy: Microstructural and electrochemical characterization*, India

[50] Kofstad P., High Temperature Corrosion, Elsevier Applied Sciesnce, Essex(1988).

[51] J. Choi, R. B. wehrspohn, J. Lee, U. Gosele, Electrochimica Acta 49, p.2645(2004)

[52] D. Gong, C. A. Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen, and E. C. Dickey, J. Mater. Res. 16, p.3331 (2001)

[53] G. K. Mor, O. K. Varghese, M. Paulose, N. Mukherjee and C. A. Grimesa,
J. Mater. Res. 18, p.2588 (2003)

[54] R. Beranek, H. Hildebrand, and P. Schmuki, Electrochemical and solid-state
letters 6, p.B12 (2003)